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None

(58) Field of search

C4P

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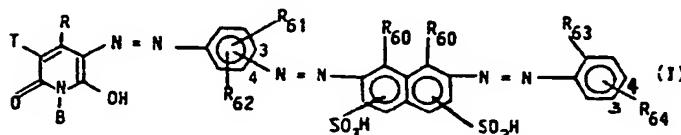
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(54) Trisazo dyes

(57) Compounds in metal-free, 1:1 or 1:2 metal complex form and in free acid or acid addition salt form, of formula I



in which R, T, B, R₆₁, R₆₂, R₆₃ and R₆₄ are hydrogen or organic radicals defined in the Specification, and one R₆₀ is OH the other being NH₂.

The compounds of formula I are useful as dyestuffs for dyeing textile materials, paper and leather.

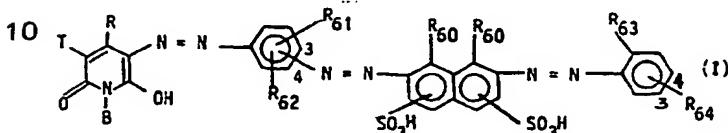
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SPECIFICATION

Improvements in or relating to organic compounds

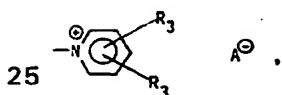
5 The invention relates to basic sulpho-containing polyazo compounds.

According to the invention there is provided a compound in metal-free, 1:1 or 1:2 metal complex form and in free acid or addition salt form, of formula I



15 in which R is hydrogen; C₁₋₄alkyl; C₅₋₆cycloalkyl unsubstituted or substituted by one or two C₁₋₄alkyl groups; phenyl, benzyl or phenyl-ethyl, the phenyl group of the latter three substituents being unsubstituted or substituted by one or two groups selected from methyl, ethyl, methoxy and ethoxy,

20 T is hydrogen; -CN,



-COOR₄; -CON(R₅)₂; -SO₂N(R₅)₂;



40 -A₂-N(R₈)₂R₉ A⁻ or -N(R₇)₂;

45 where X₄ is -O-, -N(R₆) or -S-;

R₃ is hydrogen, C₁₋₄alkyl, -N(R₅)₂ or -CON(R₅)₂;

R₄ is C₁₋₆alkyl or phenyl-C₁₋₃alkyl;

50 R₅ is hydrogen or C₁₋₄alkyl; or when two R₅'s are present attached to a nitrogen atom both R₅'s together with the N-atom to which they are attached may form a saturated ring which contains one to three heteroatoms;

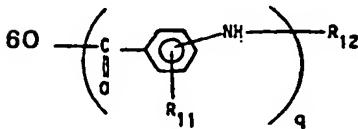
R₆ is C₁₋₄alkyl;

A is C₂₋₈alkylene which may be interrupted by up to two heteroatoms; C₂₋₈alkenylene which may be interrupted by up to two heteroatoms, phenylene or cyclohexylene;

55 A₁ is C₂₋₈alkylene or C₂₋₈alkenylene;

A₂ is C₁₋₈alkylene or C₂₋₈alkenylene;

R₂ is

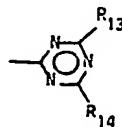


q is 0 or 1;

R₁₁ is hydrogen, halogen, NO₂, OH, C₁₋₄alkyl or C₁₋₄alkoxy

R₁₂ is

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-CO(CH₂)₈-Z,

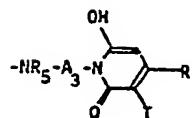
or R₂ is hydrogen,

15 a is an integer 1 to 3,

R₁₄ is an aliphatic, cycloaliphatic, aromatic or heterocyclic amine group in which the N-atom is attached to the triazinyl ring;

R₁₃ has a significance of R₁₄ or is halogen, OH, -NH₂, C₁₋₄alkoxy, phenyl or

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A₃ is a linear or branched C₂₋₆alkylene or NH-CO-CH₂- where the starred N-atom is attached to the -NR₅ group;

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Z is -N(R₇)₂ or -N(r₈)₂R₉ A⁹

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each R₇, independently, is hydrogen, C₁₋₆alkyl, C²⁻⁶alkyl substituted by an halogen, -OH or -CN group, phenyl(C₁₋₃)alkyl, the phenyl ring of which is unsubstituted or substituted by 1 to 3 groups selected from halogen, C₁₋₄alkyl and C₁₋₄alkoxy; or C₅₋₆cycloalkyl, unsubstituted or substituted by 1 or 3 C₁₋₄alkyl groups;

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or both R₇'s together with the N-atom to which they are attached form a 5- or 6-membered saturated ring which contains one to three heteroatoms (referred to hereafter as the "cyclic significances of R₇'");

each R₈, independently, has one of the non-cyclic significances of R₇ except hydrogen and R₉ is C₁₋₄alkyl unsubstituted or substituted by phenyl or

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both R₈'s, R₉ and the N-atom to which they are attached form a pyridinium group (attached by its N-atom) unsubstituted or substituted by one or two C₁₋₄alkyl groups; or a 5- or 6-membered saturated ring which contains 1 to 3 heteroatoms unsubstituted or substituted by one or two C₁₋₄alkyl groups;

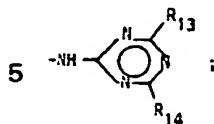
one R₆₀ is OH and the other R₆₀ is -NH₂;

R₆₁ is hydrogen, C₁₋₄alkoxy or OH;

R₆₂ is hydrogen, halogen, nitro, C₁₋₄alkyl, C₁₋₄alkoxy or OH;

R₆₃ has a significance of R₆₂ independently of R₆₂;

R₆₄ is hydrogen



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-N(R₇)₂; $\overset{\oplus}{N}(R_8)_2R_9 A^\ominus$; -COY₂-Z;

10 -CONH-Y₂-Z; -Y₂ Z; NH-CO-Y₂-Z;
-SO₂-NH-Y₂-Z or -NHNHCOCH₂-Z;
Y₂ is C₁₋₈alkylene; and
A[⊖] is a non-chromophoric anion

with the provisos that

15 (i) the number of cationic and protonatable basic groups exceeds the number of sulpho groups present by at least one;
(ii) that R₆₄ is in the 3- or 4-position on the phenyl ring to which it is attached (the positions being as indicated).
Preferably with B is -A-NH-R₂ then B is sulpho-free.

20 In the specification halogen means fluorine, chlorine, bromine or iodine, preferably chlorine.
Where any symbol appears more than once in a formula unless indicated to the contrary its significances are independent of one another.
Any alkyl, alkylene or alkenylene present is linear or branched unless indicated otherwise. The alkyl group of any alkoxy group is linear or branched unless indicated to the contrary.

25 Any sulpho group present may be in free acid or salt form. When in salt form the $-SO_3^-$ is balanced by a cation M[⊕] (where M[⊕] is a non-chromophoric cation for example Na[⊕], K[⊕] or NH₄[⊕]) or by a protonated basic non-cationic group or by a cationic group in the molecule.

Unless otherwise indicated the preferred significance of a variable applies to that variable regardless of where the variable is set forth in the specification.

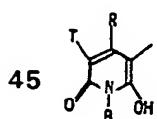
30 Any aliphatic amine group is preferably a mono(C₁₋₄alkyl)- or a di(C₁₋₄alkyl)amino group. Each alkyl group independently may be substituted by 1 to 3 substituents independently selected from halogen, phenyl, hydroxy or C₅₋₈cycloalkyl, but is preferably unsubstituted or mono substituted by phenyl or hydroxy, any hydroxy being other than in the α-position.

Any cycloaliphatic amine group present is preferably C₅₋₆cycloalkylamine, the cycloalkyl group of which may be substituted by one or two C₁₋₂alkyl groups.

35 Any aromatic amine group present is preferably aniline, the phenyl ring of which is unsubstituted or substituted by one to three substituents selected from C₁₋₄alkyl, C₁₋₄alkoxy, halogen, hydroxy and phenoxy.

Any heterocyclic amino present (or 5- or 6-membered heterocyclic ring) is preferably a

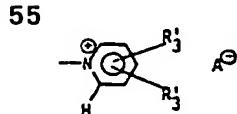
40 pyridine, triazine, pyridazine, pyrimidine, or pyrazine group or a group of the formula



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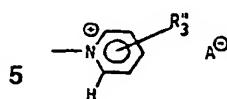
(when unsaturated) or a morpholine, pyrrolidine, piperidine, piperazine group (when saturated).

50 Each group may be substituted by one to three R₆ groups;
R is preferably R' where R' is methyl, ethyl, unsubstituted phenyl, unsubstituted benzyl or unsubstituted cyclohexyl. More preferably R is R'' where R'' is methyl or unsubstituted phenyl.
T is preferably T' where T' is hydrogen, CN,



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60 or CON(R_{5'})₂ where R_{3'} and R_{5'} are defined below. More preferably T is T'' where T'' is CN or



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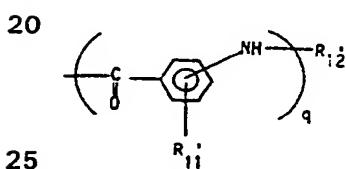
where R_3'' is defined below.

B is preferably B' where B' is $-A'-NH-R_2'$, hydrogen, $-CH_3$, $-C_2H_5$, $-C_2H_4OH$, unsubstituted cyclohexyl, benzyl, $-(CH_2)_{1-3}N(R_7')_2$; $-(CH_2)_{2-3}N(R_8')_2R_9' A^-$,

10 where the symbols are defined below. B is more preferably B'' where B'' is $-A''-NH-R_2''$, hydrogen, $-CH_3$, $-C_2H_5$, benzyl, $-(CH_2)_bN(R_7'')_2$, $-(CH_2)_bN(R_8'')_2R_9''$, where the symbols are defined below and b is 2 or 3.

B is most preferably B''' where B''' is CH_3 , C_2H_5 , benzyl, $-(CH_2)_{2-3}N(R_7'')_2$,

15 $-(CH_2)_{2-3}N(R_8'')_2R_9'' A^-$ or $A''-NH-R_2'''$. Preferably A is A' where A' is C_{2-8} -alkylene or unsubstituted phenylene. More preferably A is A'' where A'' is 1,2-ethylene, 1,3-propylene or unsubstituted meta or para phenylene. Preferably R_2 is R_2' where R_2' is a group of formula

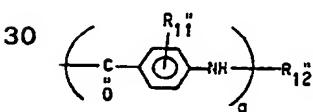


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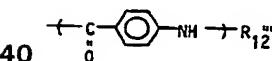
where the symbols R_{11}'' and R_{12}'' are defined below. More preferably R_2 is R_2'' where R_2'' is



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35 where R_{11}'' and R_{12}'' are defined below.
Most preferably R_2 is R_2''' where R_2''' is

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Preferably R_3 is R_3' where R_3' is hydrogen, methyl, ethyl, $-NH_2$ or $-N(CH_3)_2$. More preferably R_3 is R_3'' where R_3'' is hydrogen or methyl.

45 Preferably R_5 is R_5' where R_5' is hydrogen, methyl or ethyl. Preferably R_5' is hydrogen or methyl.

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Preferably R_6 is R_6' where R_6' is methyl or ethyl.

Preferably R_7 is R_7' where R_7' is hydrogen, linear or branched C_{1-8} -alkyl, unbranched hydroxy C_{2-3} -alkyl, benzyl, 2-chloroethyl, 2-cyanoethyl or both R_7 's together with the N-atom to which they are attached form an unsubstituted pyrrolidine, piperidine, morpholine, piperazine or

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50 N-methylpiperazine group.

More preferably R_7 is R_7'' where R_7'' is hydrogen, methyl, ethyl or 2-hydroxyethyl or both R_7''' s together with the N-atom to which they are attached form an unsubstituted morpholine, piperidine, piperazine or N-methylpiperazine group;

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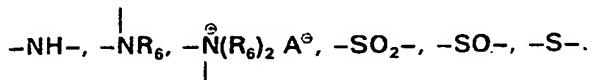
55 Preferably R_8 is R_8' where R_8' is one of the significances of R_7' except hydrogen and R_9 is R_9' where R_9' is methyl, ethyl, propyl or benzyl or both R_8' 's and R_9' together with the N-atom to which they are attached form a pyridinium ring unsubstituted or substituted by one or two methyl groups or a group β

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where Zo is $-O-$, direct bond, $-CH_2-$;



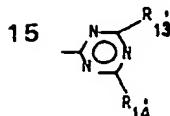
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More preferably R_8 is R_8'' where R_8'' is one of the significances of R_7'' except hydrogen and R_9 is R_9'' where R_9'' is $-\text{CH}_3$, $-\text{C}_2\text{H}_5$ or benzyl or both R_8'' 's and R_9'' together with the N-atom to which they are attached form a pyridinium ring, unsubstituted or substituted by one or two methyl groups, or is a group β defined above.

10 Preferably R_{11} is R_{11}' where R_{11}' is hydrogen, chloro, OH, nitro, methyl or methoxy. More 10
preferably R_{11} is R_{11}'' where R_{11}'' is hydrogen, methyl or chloro.

Preferably R_{12} is R_{12}' where R_{12}' is

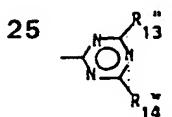


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20 or $-\text{CO}(\text{CH}_2)_{1-2}\text{Z}'$
or hydrogen;

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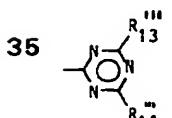
More preferably R_{12} is R_{12}'' where R_{12}'' is $\text{COCH}_2\text{Z}''$ or



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30 where R_{13}'' , R_{14}'' and Z'' are defined below.
Most preferably R_{12} is R_{12}''' where R_{12}''' is

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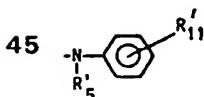


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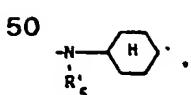
40 where R_{13}''' and R_{14}''' are defined below.

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Preferably R_{13} is R_{13}' where R_{13}' is chloro, $-\text{OH}$, $-\text{NH}_2$, OCH_3 ,



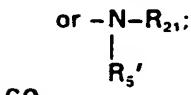
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mono C_{1-4} alkylamino, di- (C_{1-2}) alkylamino, monohydroxy (C_{2-4})alkylamino, bis-[hydroxy-(C_{2-4})alkyl]amino

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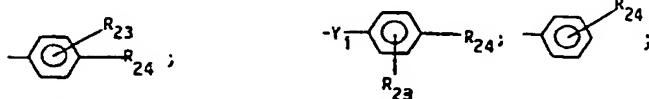
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60 where R_{21} is unsubstituted C_{1-12} alkyl; or C_{2-12} alkyl substituted by $-\text{OH}$; or C_{3-12} alkyl interrupted by one to three groups selected from

$-N(R_7)-$ and $\tilde{N}(R_8)_2 A^\ominus$; $-NHCOCH_2-Z$; $-CH_2CONH-Y_1-Z$; $-Y_1-Z$;

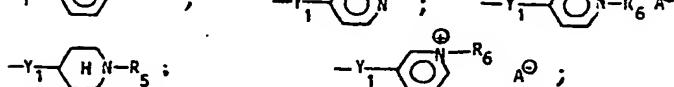
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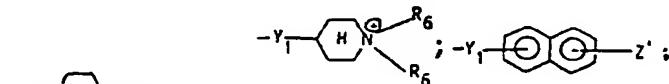
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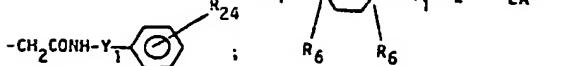
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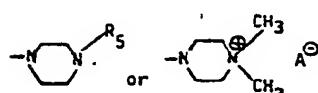
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or $-N-R_{21}$, forms a group of formula
 $\begin{array}{c} | \\ R_{21}' \end{array}$

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35 where Y_1 is a C_{1-8} alkylene or a C_{3-8} alkenylene group

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 Z is $-N(R_7)_2$ or $\tilde{N}(R_8)_2 R_9 A^\ominus$ R_{23} is halogen, $-OH$, $-NO_2$, C_{1-4} alkyl or C_{1-4} alkoxy;40 $-CONH-Y_2-Z'$, $-SO_2NH-Y_2-Z'$; $-Y_2-Z'$ or $-NHNHCOCH_2-Z'$,
where Y_2 is C_{1-8} alkylene

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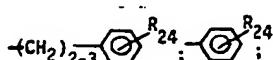
More preferably R_{13} is R_{13}'' where R_{13}'' is $-N-R_{21}'$

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45 where R_{21}' is $-(CH_2)_{2-3}-N(R_7'')-(CH_2)_{2-3}-N(R_7'')R_8'$
 $-(CH_2)_{2-3}\tilde{N}(R_8'')_2-(CH_2)_{2-3}\tilde{N}(R_8'')_2 R_6' A^\ominus$
 $-CH_2)_{2-3}-N(R_7'')-C_2H_5$

50 $-(CH_2)_{2-3}\tilde{N}(R_8'')_2 C_2H_5$

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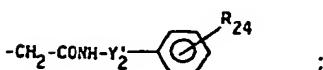
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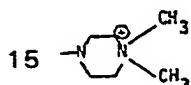
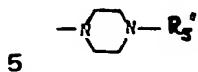
$-NHCOCH_2-Z''$
 $-CH_2-CONH-Y_2'-Z''$; $Y_2'-Z''$;

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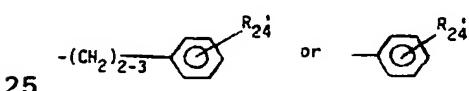
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where R_6' is methyl or ethyl
 where Y_2' is $(C_{1-4})alkylene$.
 20 Most preferably R_{21} is R_{21}'' where R_{21}'' is $-NHCOCH_2-Z'', -(CH_2)_{2-3}-Z''$



where R_{24}' is $-N(CH_3)_2$, $-N(CH_3)_3$, A' ; $-CONH(CH_2)_{2-3}Z''$, $-NHCO(CH_2)_{2-3}Z''$, $-CO(CH_2)_{2-3}Z''$ or $SO_3NH(CH_2)_{2-3}Z''$.

30 Most preferably R_{13} is R_{13}''' where R_{13}''' is $-N-R_{21}''$
|
 R_5'' .

Preferably Z is Z' where Z' is $-N(R_7')_2$ or $-N(R_8')_2 R_9' A'$.

35 More preferably Z is Z'' where Z'' is $N(R_7'')_2$ or $-N(R_8'')R_9'' A'$.

Preferably R_{14} is R_{14}' where R_{14}' is $-N-R_{21}'$. More preferably

40. R_{\perp} is R_{\perp}'' where R_{\perp}'' is $-N(R_{\perp}'')R_{\perp}'''$

Most preferably R_{14} is R_{14}''' where R_{14}''' is $-N-R_{21}''$.

45 Preferably R_{62} is R_{62}' where R_{62}' is hydrogen, chloro, nitro, methyl, methoxy or OH; more preferably R_{62} is R_{62}' where R_{62}' is hydrogen, chloro, nitro, methyl, methoxy or OH.

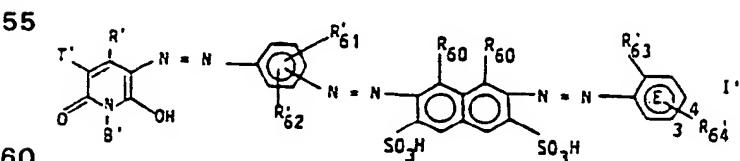
Preferably R_{62} is R_{62}' where R_{62}' is hydrogen, chloro or methyl.

Preferably R_{61} is R_{61}' where R_{61}' is hydrogen, methoxy or methyl.
 Preferably R_{63} is R_{63}' where R_{63}' is hydrogen, nitro, methoxy, ethoxy, OH, methyl, ethyl or 50 chloro.

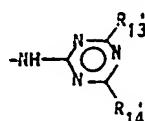
more preferably R_{c2} is R_{c2}'' where R_{c2}'' is hydrogen, OH or methoxy.

Preferred compounds of formula I are of formula I' in metal-free, 1:1 or 1:2 metal complex

reduced compounds of formula I or formula I' in metal-free, 1:1 or 1:2 metal complex form and free acid or acid addition salt form,



in which R_{64}' is



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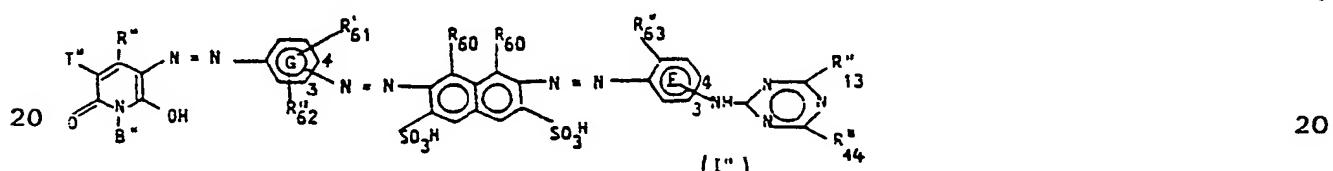
$N(R_7')_2$, $-N(R_8')_2R_9'$, A' , $-CONH-Y_2'-Z'$, $-CO-Y_2'-Z'$, $-Y_2'-Z'$, $-SO_2-NHY_2'-Z'$,
 $-NHCOY_2'-Z'$, $NHNYCOCH_2-Z'$;

and the other symbols are as defined above;
with the provisos that:

10 (i) the number of cationic and protonatable basic groups exceeds the number of sulpho groups present by at least one;
(ii) that R_{64}' is in the 3- or 4-position on the phenyl ring to which it is attached (the positions being as indicated).

More preferred compounds of formula I are of formula I'' in metal-free, 1:1 or 1:2 metal complex form

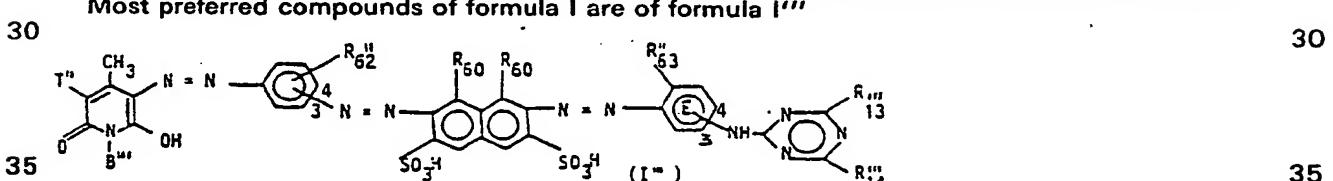
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in which the symbols are as defined above, with the provisos that

(i) the number of cationic and protonatable basic group exceeds the number of sulpho groups present by at least one;
(ii) that the amino group on ring E is in the 3- or 4-position (the positions being as indicated);
(iii) that the azo group on ring G is in the 3- or 4-position (the positions being as indicated). Most preferred compounds of formula I are of formula I'''

20



in which T'' , R_{62}'' , R_{60} , R_{63}'' , B''' , R_{13}''' and R_{14}''' are defined above;
with the provisos that

(i) the number of cationic and protonatable basic groups exceeds the number of sulpho groups present by at least one;
(ii) that the amino group on ring E is in the 3- or 4-position (the positions being as indicated);
(iii) that the azo group on ring G is in the 3- or 4-position (the positions being as indicated).

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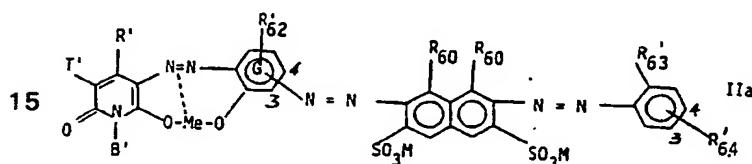
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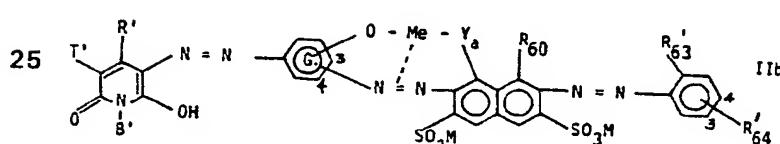
in which each A_5 independently, is $-O-$ or $-NH-$
 Me_3 is a 1:1 or 1:2 metal complex forming metal;
both R_{66} 's and R_{67} 's are ortho to each other and together form an aromatic ring system (for
example together with the two carbon atoms to which they are attached form a
5  group).

10 Preferred compounds of formula I when in metallised form are of formulas IIa to IIe

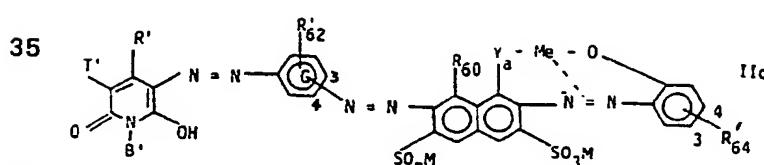


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where Y₁ is =O= or =NH=

45 M₁ is Cu, Cr, Co, Ni, Fe, Mn or Zn for 1:1 metal complexes (Me is preferably copper in this case) or Me is chromium, cobalt, iron or nickel for 1:2 metal complexes (Me is preferably iron in this case); and the other symbols are defined above; with the proviso that

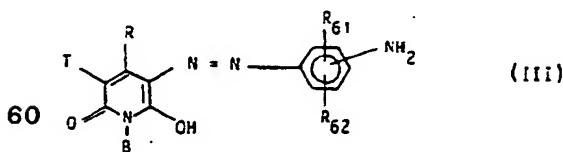
(i) in the compounds of formula IIa, IIb and IIc R_{64'} is in the 3- or 4-position, the naphthyl group on ring G is in the 3- or 4-position and the number of cationic and protonatable basic groups present exceeds the number of sulphe groups.

(ii) in the compounds of formula IIb the group $-O-Me-Ya-$ is ortho to the naphthyl azo group; and

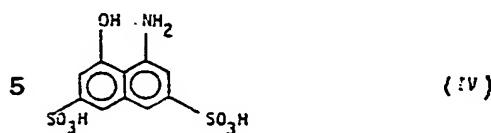
(iii) in the compounds of formula IIb and IIc when Y_1 is $-\text{NH}-$ then R_{60} is OH and when Y_1 is $-\text{O}-$ then R_{60} is NH_2 .

Compounds of formula I in metal-free form may be prepared by either reacting a diazotised compound of formula III

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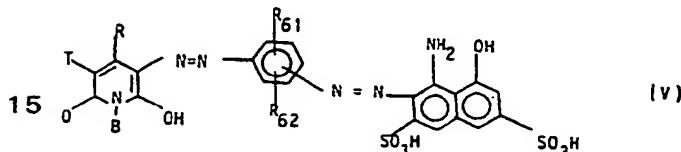
with a compound of the formula IV



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10 in acid medium to form a compound of formula V

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20 followed by reacting the compound of formula V with a diazotised compound of formula IV

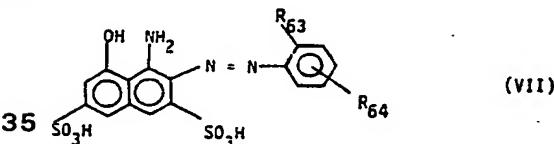
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30 in alkali medium; or
by reaction a diazotised compound of formula IV with the compound of formula IV to form a compound of formula VII

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40 in acid medium followed by reacting the compound of formula VII with a diazotised compound of formula III in alkali medium. The SO3H groups can be converted to the salt form by known methods.

40 Coupling to form compounds of formula I can be carried out according to known methods. Advantageously, coupling is carried out in aqueous (acid, neutral or alkali) medium at a temperature from -10°C to room temperature, if necessary in the presence of a coupling accelerator such as pyridine or urea. Alternatively, coupling may be effected in a mixture of solvents, for example, water and an organic solvent.

45 Metallisation of the compounds of formula I can be achieved by known methods.

The azo compounds of formula I in 1:1 metal complex form may be prepared by metallising compounds of formula I in metal-free form with a metal selected from copper, cobalt, iron, nickel, manganese, chromium and zinc.

50 The azo compounds of formula I in 1:2 metal complex form may be prepared by metallising compounds of formula I in metal-free form with a metal selected from chromium, nickel, cobalt and iron.

55 Metallisation is carried out advantageously in aqueous medium or a mixture of water and a water-miscible organic solvent, for example acetone, lower alkyl alcohols, dimethylformamide, formamide, glycols or acetic acid at a pH range from 1.0 to 8.0, preferably pH 2 to 7. The metallisation process may be carried out at a temperature from room temperature to the boiling point of the reaction medium.

60 Alternatively, metallisation may be effected in a wholly organic medium (for example dimethylformamide). Advantageously, for instance, cobaltisation may be carried out in the presence of an inorganic nitrite such as lithium, sodium, ammonium or potassium nitrite in the ratio of 2 to 6 moles of nitrite per gram atom of cobalt.

Suitable cobalt-yielding compounds are, for example, cobalt (II or Co (III)) sulphate, acetate, formate or chloride.

Copper-yielding compounds are, for example, cupric sulphate, cupric formate, cupric acetate and cupric chloride.

65

The nickel-yielding compounds are Ni (II) or Ni (III) compounds, such as nickel formate, nickel acetate and nickel sulphate.

Preferred manganese-yielding compounds are Mn (II) compounds and iron-yielding compounds are Fe (II) or Fe (III) compounds. Examples of these and zinc-yielding compounds are 5 manganese, iron and zinc formate, acetate and sulphate.

Preferred chromium-yielding compounds are Cr (II) and Cr (III) formate, acetate and sulphate.

In the compounds of formula I the anions A³⁻ can be any non-chromophoric anions such as those conventional in basic dyestuff chemistry. Suitable anions include chloride, bromide, sulphate, bisulphate, methylsulphate, aminosulphonate, perchlorate, benzenesulphonate, oxalate, maleate, acetate, propionate, lactate, succinate, tartrate, malate, methanesulphonate and benzoate, as well as complex anions, for example, zinc chloride double salts and anions of boric acid, citric acid, glycollic acid, diglycollic acid and adipic acid or addition products of orthoboric acid with polyalcohols with at least one *cis* diol group present. These anions can be exchanged for each other by ion exchange resins or by reaction with acids or salts (for example via the 10 hydroxide or bicarbonate or according to German Offenlegungsschrift 2,001,748 or 15 2,001,816).

The azo compounds of formula I are suitably worked up into solid or liquid preparations, for example by granulation or by dissolving in a suitable solvent. The compounds of formula I are suitable for dyeing, padding or printing on fibres, threads or textile materials particularly natural 20 or regenerated cellulose materials for example cotton, or synthetic polyamides or synthetic polyesters in which the acid groups have been modified. Such a polyamide is described in Belgian Patent 706,104 and such a synthetic polyester is described in US Patent 3,379,723.

The azo compounds of formula I may also be applied to base fibres such as hemp, flax, sisal, jute, coir or straw.

25 The azo compounds of formula I are also used for dyeing, padding or printing fibres, threads or textiles produced therefrom which consist of or contain homo- or mixed polymers of acrylonitrile or a 1,1-dicyanoethylene.

The textile material is dyed, printed or pad-dyed in accordance with known methods. Acid modified-polyamide is dyed particularly advantageously in an aqueous, neutral or acid medium, 30 at temperatures of 60°C to boiling point or at temperatures above 100°C under pressure.

The textile material may also be dyed by the compounds of formula I in organic solvents, e.g. in accordance with the directions given in German Offenlegungsschrift 2,437,549.

Cellulose material is mainly dyed by the exhaust process, i.e. from a long or short bath, at room temperature to boiling temperature, optionally under pressure, whereby the ratio of the 35 bath is from 1:1 to 1:100 and preferably from 1:20 to 1:50. If dyeing is effected from a short bath, then the liquor ratio is 1:5 to 1:15. The pH of the dye bath varies between 3 and 10 (for short and long dyebaths). Dyeing preferably takes place in the presence of electrolytes.

Printing may be effected by impregnation with a printing paste produced by known methods.

The dyes of formula I are also suitable for dyeing or printing paper, e.g. for the production of 40 bulk-dyed, sized and unsized paper. The dyestuffs may similarly be used for dyeing paper by the dipping process. The dyeing of paper is effected by known methods.

The dyes of formula I are also suitable for dyeing or printing leather by known methods.

Dyeings with good fastness are obtained on both paper and leather.

Dyeings made with the dyes of formula I on leather have good light fastness properties, good 45 diffusion properties with PVC, good water-, wash and sweat-fastness properties, good fastness to dry cleaning, good fastness to drops of water and good fastness to hard water.

Dyeings prepared with dyes of formula I

on paper produce a substantially clear spent liquor which is important for environmental 50 reasons. The dyes of formula I have good build-up properties, do not run once applied to paper and are not pH sensitive. Dyeings produced with dyes of formula I have good light fastness and the nuance on exposure for a long time to light fades tone in tone. The dyes of formula I have good wet fastness properties not only for water but also for milk, soap, water, sodium chloride solution, fruit juice, and sweetened mineral water. Further dyeings made with dyes of formula I are fast for alcoholic beverages due to a good alcohol fastness. Further the dyes of formula I 55 have good nuance stability.

The dyes of formula I may be converted into dyeing preparations. Processing into stable liquid or solid dyeing preparations may take place in a generally known manner, advantageously by grinding or granulating or by dissolving in suitable solvents, optionally adding an assistant, e.g. a stabiliser or dissolving intermediary such as urea. Such preparations may be obtained, for 60 example, as described in French Patent Specification 1,572,030 and 1,581,900 or in accordance with German DOS 2,001,748 and 2,001,816.

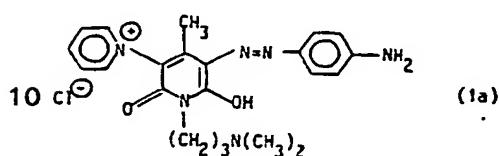
Liquid preparations of the compounds of formula I preferably comprise 10 to 30% by weight of a compound of formula I and to 30% of a solubilising agent such as urea, lactic acid or acetic acid, the rest of the composition being water. Solid preparations preferably comprise 20 65 to 80% dyestuff, 20 to 80% solubilising agent such as urea or Na₂SO₄ and 2 to 5% water.

In the following Examples all parts and percentages given are by weight and the temperatures given are in degrees Centigrade, unless indicated to the contrary.

Example 1

5 In 600 parts of water 22.2 parts (0.05 mols) of a compound of the formula 1a

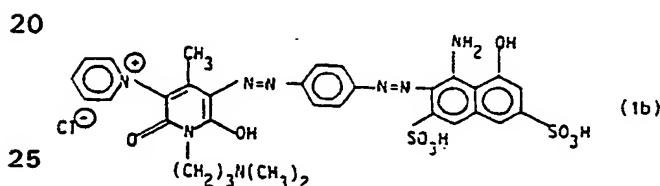
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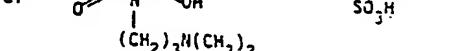
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15 in hydrochloric acid medium are diazotised with 3.45 parts (0.05 mols) of sodium nitrite at 0–5°. To this solution 15.9 parts (0.05 mols) of 1 amino-8-hydroxy naphthalene-3,6-disulphonic acid are added dropwise, dissolved in 150 parts of water and 3 parts of sodium carbonate. The solution has a pH of 1.5. By the addition of 10 parts of sodium acetate over 12 hours the pH is brought to 2.3. The resulting dyestuff is of formula 1b

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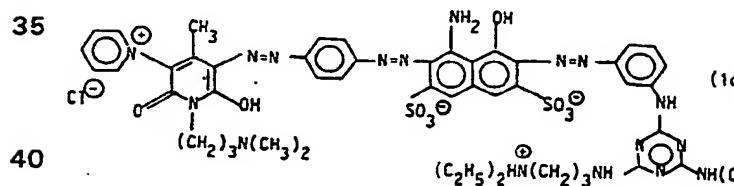
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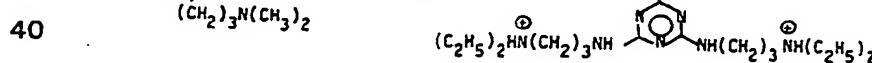
30 22 Parts (0.05 mols) of 2,4 bis-(diethylaminopropylamino)-6-(3'-aminophenylamino)-5-triazine in hydrochloric acid medium are diazotised in aqueous medium with 3.45 parts (0.05 mols) of sodium nitrite at 0–5° and are then added to the compound of formula 1b in acid medium.

30

By the addition of 45 parts of a 30% aqueous NaOH solution the pH is brought to 8.5 to 9. After coupling has finished a dyestuff of the formula 1c



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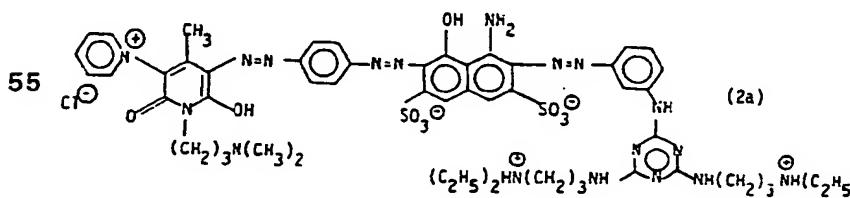
is obtained. This compound 1c dyes paper and leather a black tone.

45 *Example 2*

45

22 Parts (0.05 mols) of 2,4-bis(diethylamino propyl amino)-6-(3'-amino phenylamino)-3-triazine in hydrochloric acid medium are diazotised in aqueous medium with 3.45 parts (0.05 mols) of sodium nitrite at 0.5°. This is then added in acid medium to 1-amino-8-hydroxy naphthalene 3,6-disulphonic acid and then 22.2 parts of the compound of formula 1a (from Example 1) are added in alkali medium to produce the compound of formula 2a

50



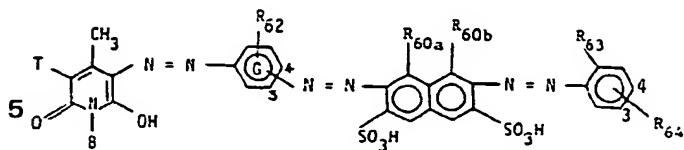
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60 This is an isomeric form of the compound 1c and also dyes paper and leather a black tone. Both dyes 1c and 2a have good fastness properties.

60

Examples 3 to 25
65 Compounds of the formula

65



in which the symbols are defined in Table 1 can be formed by a method analogous to that of Example 1 or Example 2 from appropriate starting materials. In these Examples the symbols
10 A_{33-42} and T_2 , T_4 and T_5 are as defined below.

10

A₃₃ is $-(CH_2)_3N(CH_3)_2$ A₃₄ is $-(CH_2)_2NH_2$ 15 A₃₅ is $-(CH_2)-NH-\begin{array}{c} \text{N} \\ | \\ \text{N}=\text{N}-\end{array}$

15

20 A₃₆ is $-(CH_2)_2-NH-\begin{array}{c} \text{NH}(CH_2)_3N(C_2H_5)_2 \\ | \\ \text{N}=\text{N}-\end{array}$

20

A₃₇ is $-(CH_2)_2NHCOCH_2-\begin{array}{c} \text{N} \\ | \\ \text{N}-\text{C}_2\text{H}_4\text{NH}_2 \end{array}$ 25 A₃₈ is $-NH-\begin{array}{c} \text{N} \\ | \\ \text{N}=\text{N}-\end{array}$

25

30 A₃₉ is $-NH-\begin{array}{c} \text{N} \\ | \\ \text{N}-\text{C}_2\text{H}_4\text{NH}_2 \end{array}$

30

35 A₄₀ is $-NHCOCH_2-\overset{\oplus}{N}(\text{CH}_3)_3 \text{Cl}^{\ominus}$

35

40 A₄₁ is $-CONH(CH_2)_3N(CH_3)_2$

40

A₄₂ is $-SO_2NH(CH_2)_2N(C_2H_5)_2$ T₂ represents $-CN$ 45 T₄ do. $\begin{array}{c} \oplus \\ \text{N} \\ | \\ \text{C}_6\text{H}_4 \end{array} A^{\ominus}$

45

T₅ do. $\begin{array}{c} \oplus \\ \text{N} \\ | \\ \text{C}_6\text{H}_4 \\ \text{CH}_3 \end{array} A^{\ominus}$

Table 1b

| 5 | Ex. No. | T | B | Positions and sig- nificance of R ₆₂ | Position of -N = N on ring G | R _{60a} | R _{60b} | R ₆₃ | Position and significance of R ₆₄ | 5 |
|----|------------|----------------|-----------------|--|---------------------------------------|------------------|------------------|------------------|--|----|
| 10 | 3 | T ₄ | A ₃₃ | H | 4 | OH | NH ₂ | H | 4-A ₃₈ | |
| | 4 | T ₄ | do. | H | 4 | NH ₂ | OH | H | 4-A ₃₈ | |
| | 5 | T ₄ | do. | H | 3 | OH | NH ₂ | H | 3-A ₃₈ | 10 |
| | 6 | T ₄ | do. | H | 3 | NH ₂ | OH | H | 3-A ₃₈ | |
| | 7 | T ₄ | do. | H | 3 | OH | NH ₂ | H | 3-A ₃₈ | |
| | 8 | T ₄ | do. | H | 3 | NH ₂ | OH | H | 4-A ₃₈ | |
| 15 | 9 | T ₂ | A ₃₅ | H | 4 | OH | NH ₂ | H | 3-A ₃₈ | 15 |
| | 10 | T ₅ | do. | H | 4 | OH | NH ₂ | H | 3-A ₃₈ | |
| | 11 | T ₄ | A ₃₄ | H | 4 | OH | NH ₂ | H | 3-A ₃₈ | |
| 20 | 12 | T ₄ | A ₃₅ | H | 4 | OH | NH ₂ | H | 3-A ₃₈ | |
| | 13 | T ₄ | A ₃₆ | H | 4 | OH | NH ₂ | H | 3-A ₃₈ | 20 |
| | 14 | T ₄ | A ₃₇ | H | 4 | OH | NH ₂ | H | 3-A ₃₈ | |
| | 15 | T ₄ | A ₃₅ | H | 4 | OH | NH ₂ | H | 3-A ₃₉ | |
| 25 | 16 | T ₄ | do. | H | 4 | OH | NH ₂ | H | 3-A ₄₀ | |
| | 17 | T ₄ | do. | H | 4 | OH | NH ₂ | H | 3-A ₄₁ | 25 |
| | 18 | T ₄ | do. | H | 4 | OH | NH ₂ | H | 3-A ₄₂ | |
| | 19 | T ₄ | A ₃₃ | OH(4) | 3 | OH | NH ₂ | H | 3-A ₃₈ | |
| 30 | 20 | T ₄ | do. | OH(4) | 3 | OH | NH ₂ | H | 3-A ₃₈ | |
| | 21 | T ₄ | do. | OH(3) | 4 | OH | NH ₂ | H | 3-A ₃₈ | |
| | 22 | T ₄ | do. | OH(3) | 4 | OH | NH ₂ | H | 3-A ₃₈ | 30 |
| | 23 | T ₄ | A ₃₅ | H | 4 | NH ₂ | OH | OH | 3-A ₄₂ | |
| | 24 | T ₄ | do. | H | 4 | NH ₂ | OH | OH | 3-A ₄₂ | |
| | 25 | T ₄ | do. | H | 4 | NH ₂ | OH | OCH ₃ | 3-A ₄₂ | |

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Examples 26 to 28

The following metallised compounds can be formed by metallising the appropriate compounds:

40 Example 26 : 1:1 copper complex of Example 20
 Example 27 : 1:1 copper complex of Example 22
 Example 28 : 1:1 copper complex of Example 24.

40

The compounds of Examples 3, 4, 9 to 19 and 21 to 28 are black and the compounds of
 45 Examples 5 to 8 and 20 are greenish-black.

45

Application Example A

70 Parts of chemically bleached sulphite cellulose obtained from pinewood and 30 parts of
 50 chemically bleached sulphite cellulose obtained from birchwood are ground in 2000 parts of
 water in a Hollander. 0.12 Parts of the dyestuff from Example 1 of formula 1c are sprinkled into
 this pulp. Paper is produced from this pulp after mixing for 20 minutes. The absorbent paper
 which is obtained in this manner is dyed in a black tone. The waste water is practically
 colourless.

50

55 Application Example B

0.5 Parts of the dyestuff from Example 1 of formula 1c are added to 100 parts of chemically
 bleached sulphite cellulose which have been ground in a Hollander with 2000 parts of water
 Sizing takes place after thorough mixing for 15 minutes. The paper which is produced from this
 material has a black tone and good light- and wet-fastnesses.

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Application Example C

An absorbent length of unsized paper is drawn at 40 to 50°C through a dyestuff solution
 having the following composition:

65 0.5 Parts of the dyestuff from Example 1

65

0.5 Parts of starch and
99.0 Parts of water.

The excess dyestuff solution is squeezed out through two rollers. The dried length of paper is
5 dyed in a black tone. 5

Application Example D

100 Parts freshly tanned and neutralised chrome leather are agitated for 30 minutes in a vessel with a dye bath of 250 parts water at 55°C and 0.5 parts of the dyestuff of Example 1,
10 and then treated in the same bath for 30 minutes with 2 parts of an anionic fatty liquor based on sulphonated train oil. The leather is then dried and prepared in the normal way, giving a 10 leather evenly dyed in a black tone.

Other low affinity vegetable-tanned leathers can similarly be dyed by known methods.

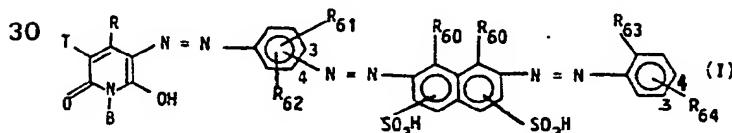
15 *Application Example E*

2 Parts of the dyestuff of Example 1 are dissolved in 4000 parts demineralised water at 40°C. 15
100 parts of a prewetted cotton textile substrate are added, and the bath is raised to boiling point over 30 minutes and held at the boil for 1 hour. After rinsing and drying, a black dyeing is obtained having good light- and wet-fastnesses. The dye exhausts practically totally and the
20 waste water is almost colourless.

The dyestuffs of any of the other Examples 2 to 28 may be used in place of the compound of Example 1 any one of Application Examples A to C. The dyes so used may be in the form of solid or liquid preparations. 20

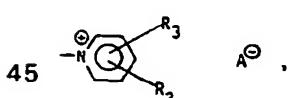
25 CLAIMS

1. A compound in metal-free, 1:1 or 1:2 metal complex form and in free acid or acid addition salt form, of formula I 25



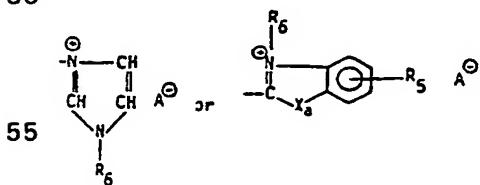
35 in which R is hydrogen; C_{1-4} alkyl; C_{5-6} cycloalkyl unsubstituted or substituted by one or two C_{1-4} alkyl groups; phenyl, benzyl or phenyl-ethyl, the phenyl group of the latter three substituents being unsubstituted or substituted by one or two groups selected from methyl, ethyl, methoxy and ethoxy, 35

40 T is hydrogen; -CN, 40



-COOR₄; -CON(R₅)₂; -SO₂N(R₅)₂;

50



B is -A-NH-R₂; hydrogen; C_{1-4} alkyl unsubstituted or substituted by a C_{1-4} alkoxy, C_{2-4} alkyl substituted by hydroxy; C_{5-6} cycloalkyl unsubstituted or substituted by one to three C_{1-4} alkyl groups; phenyl C_{1-3} alkyl, the phenyl group of which is unsubstituted or substituted by one to three groups selected from C_{1-4} alkyl, C_{1-4} alkoxy and halogen; -A₁-N(R₇)₂; 60

-A₂-N(R₈)₂R₉A⁺ or -N(R₅)₂;

where X_a is -O-, -N(R₅) or -S-;

65 R₃ is hydrogen, C_{1-4} alkyl, -N(R₅)₂ or -CON(R₅)₂; 65

R₄ is C₁₋₆alkyl or phenyl-C₁₋₃alkyl;

R₅ is hydrogen or C₁₋₄alkyl; or when two R₅'s are present attached to a nitrogen atom both R₅'s together with the N-atom to which they are attached may form a saturated ring which contains one to three heteroatoms;

5 R₆ is C₁₋₄alkyl;

A is C₂₋₈alkylene which may be interrupted by up to two heteroatoms; C₂₋₈alkenylene which may be interrupted by up to two heteroatoms, phenylene or cyclohexylene;

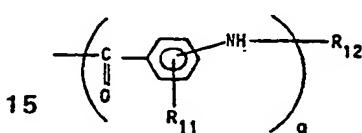
A₁ is C₂₋₈alkylene or C₂₋₈alkenylene;

A₂ is C₁₋₈alkylene or C₂₋₈alkenylene;

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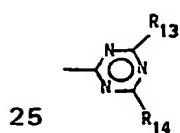


15

q is 0 or 1;

20 R₁₁ is hydrogen, halogen, NO₂, OH, C₁₋₄alkyl or C₁₋₄alkoxy

20



25

-CO(CH₂_n-Z,

or R₂ is hydrogen,

30 a is an integer 1 to 3,

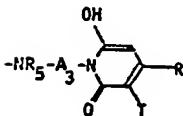
30

R₁₄ is an aliphatic, cycloaliphatic, aromatic or heterocyclic amine group in which the N-atom is attached to the triazinyl ring;

R₁₃ has a significance of R₁₄ or is halogen, OH, -NH₂, C₁₋₄alkoxy, phenyl or

35

35



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40

A₃ is a linear or branched C₂₋₆alkylene or -NH-CO-CH₂- where the starred N-atom is attached to the -NR₅ group;

Z is -N(R₇)₂ or -³N(R₈)₂R₈A⁶

45

45

each R₇, independently, is hydrogen, C₁₋₆alkyl, C₂₋₆alkyl substituted by an halogen, -OH or -CN group, phenyl(C₁₋₃)alkyl, the phenyl ring of which is unsubstituted or substituted by 1 to 3 groups selected from halogen, C₁₋₄alkyl and C₁₋₄alkoxy; or C₅₋₈cycloalkyl, unsubstituted or substituted by 1 or 3 C₁₋₄alkyl groups;

45

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or both R₇'s together with the N-atom to which they are attached form a 5- or 6-membered saturated ring which contains one to three heteroatoms (referred to hereafter as the "cyclic significances of R₇'");

each R₈, independently, has one of the non-cyclic significances of R₇ except hydrogen and R₉ is C₁₋₄alkyl unsubstituted or substituted by phenyl or

50

55

55

both R₈'s, R₉ and the N-atom to which they are attached form a pyridinium group (attached by its N-atom) unsubstituted or substituted by one or two C₁₋₄alkyl groups; or a 5- or 6-membered saturated ring which contains 1 to 3 heteroatoms unsubstituted or substituted by one or two C₁₋₄alkyl groups;

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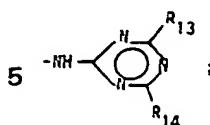
one R₆₀ is OH and the other R₆₀ is -NH₂;

R₆₁ is hydrogen, C₁₋₄alkoxy or OH;

R₆₂ is hydrogen, halogen, nitro, C₁₋₄alkyl, C₁₋₄alkoxy or OH;

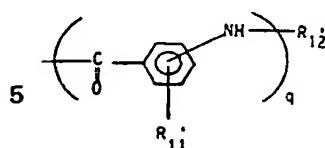
R₆₃ has a significance of R₆₂ independently of R₆₂;

R₆₄ is hydrogen



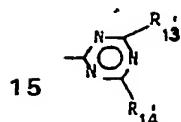
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| | | |
|----|--|----|
| 10 | $-N(R_7)_2$; $-\overset{\oplus}{N}(R_8)_2 R_9 A^\ominus$; $-COY_2-Z$; $-CONH-Y_2-Z$; $-Y_2-Z$; $NH-CO-Y_2-Z$; $-SO_2-NH-Y_2-Z$ or $-NHNC(=O)CH_2-Z$; Y_2 is C_{1-8} alkylene; and A^\ominus is a non-chromophoric anion with the provisos that | 10 |
| 15 | (i) the number of cationic and protonatable basic groups exceeds the number of sulpho groups present by at least one; (ii) that R_{64} is in the 3- or 4-position on the phenyl ring to which it is attached (the positions being as indicated). | 15 |
| 20 | 2. A compound according to Claim 1 in which R is R' where R' is methyl, ethyl, unsubstituted phenyl, unsubstituted benzyl or unsubstituted cyclohexyl. 3. A compound according to Claim 1 in which R is R'' where R'' is methyl or unsubstituted phenyl. 4. A compound according to any one of the preceding claims in which T is T' where T' is hydrogen, CN; | 20 |
| 25 |  | 25 |
| 30 | where R_3' is hydrogen, methyl, ethyl, $-NH_2$ or $N(CH_3)_2$, and R_5' is hydrogen, methyl or ethyl. 5. A compound according to Claim 4 in which T is T'' where T'' is CN or | 30 |
| 35 |  | 35 |
| 40 | where R_3'' is hydrogen or methyl. 6. A compound according to any one of the preceding claims in which B is B' where B' is $A'-NH-R_2'$, hydrogen, $-CH_3$, $-C_2H_5$, $-C_2H_4OH$, unsubstituted cyclohexyl, benzyl, $-(CH_2)_{1-3}N(R_1')$, $-(CH_2)_{2-3}\overset{\oplus}{N}(R_8')_2 R_9' A^-$, where A' is C_{2-8} alkylene or unsubstituted phenylene, R_1' is hydrogen, linear or branched C_{1-6} alkyl, unbranched hydroxy C_{2-3} alkyl, benzyl, 2-chloroethyl, 2-cyanoethyl or both R_1' 's together with the N-atom to which they are attached form an unsubstituted pyrrolidine, piperidine, morpholine, piperazine or N-methylpiperazine group; R_8' is one of the significances of R_1' except hydrogen and R_9' is methyl, ethyl, propyl or benzyl or both R_8' 's and R_9' ' together with the N-atom to which they are attached form a pyridinium ring unsubstituted or substituted by one or two methyl groups or a group β | 40 |
| 45 |  | 45 |
| 50 | 55 where Zо is $-O-$, direct bond, $-CH_2-$; | 50 |
| 55 | $-NH-$, $-NR_6$, $-\overset{\oplus}{N}(R_8)_2 A^-$, $-SO_2-$, $-SO-$, $-S-$, and R_2' is a group of formula | 55 |
| 60 | $ $ $-NH-$, $-NR_6$, $-\overset{\oplus}{N}(R_8)_2 A^-$, $-SO_2-$, $-SO-$, $-S-$, and R_2' is a group of formula | 60 |



q is defined in Claim 1;
10 R_{11'} is hydrogen, chloro, OH, nitro, methyl or methoxy; R_{12'} is

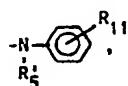
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or -CO(CH₂)₁₋₂-Z' or hydrogen;
R_{13'} is chloro, OH, -NH₂, OCH₃,

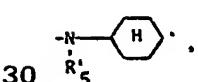
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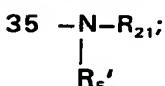


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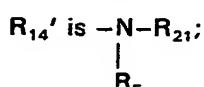


mono C₁₋₄alkylamino, di(C₁₋₂)alkylamino, monohydroxy(C₂₋₄)alkylamino, bis-[hydroxy(C₁₋₄)alkyl]amino or



40 Z' is -N(R_{7'})₂ or $\overset{\oplus}{N}(R_8')_2 R_{99'} A^\ominus$;

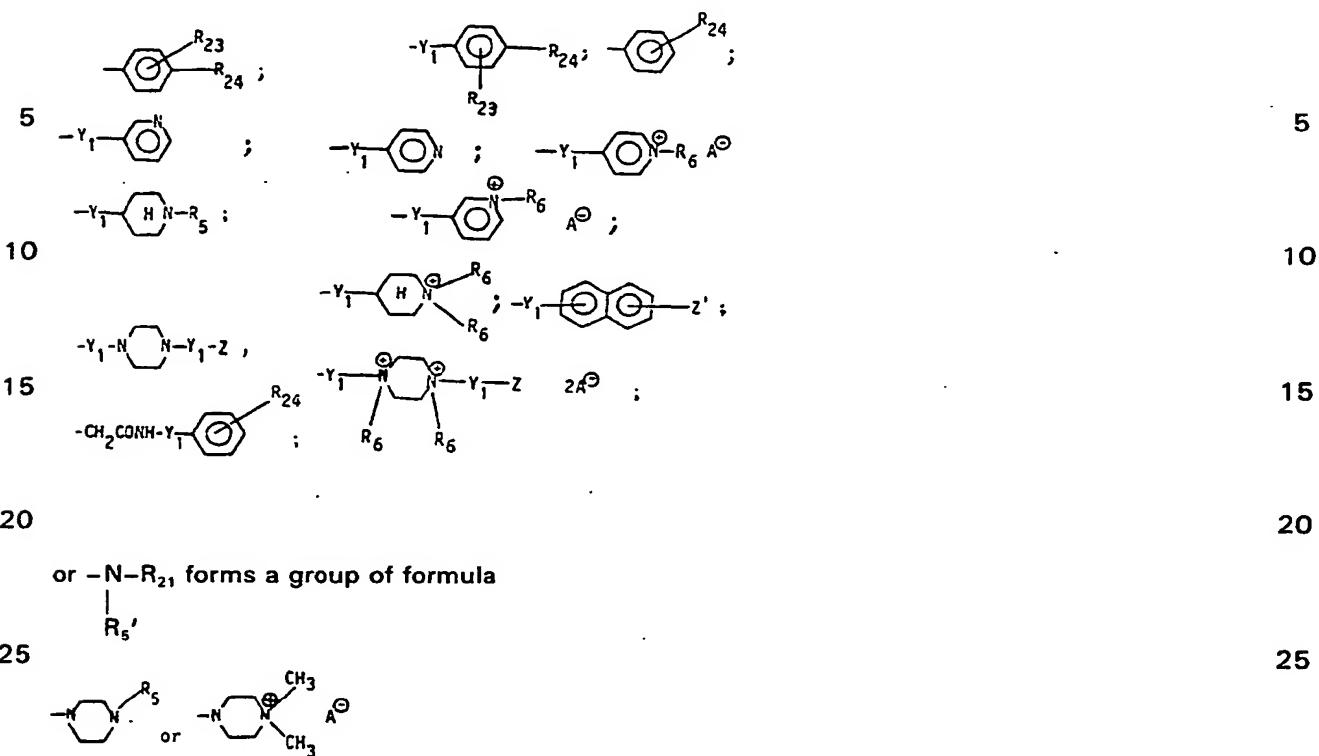
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45 where R₂₁ is unsubstituted C₁₋₁₂alkyl; or C₂₋₁₂alkyl substituted by -OH; or C₃₋₁₂alkyl interrupted by one to three groups selected from

45





³⁰ where Y₁ is a C₁₋₈alkylene or a C₃₋₈alkenylene group 30

Z is $-N(R_7)_2$ or $-N(R_8)_2 R_9 A^+$

30 where Y_1 is a C_{1-8} alkylene or a C_{3-8} alkenylene group
 Z is $-N(R_7)_2$ or $-N(R_8)_2 R_9 A'$
 R_7 is halogen, $-OH$, $-NO_2$, alkyl or C_{2-8} alkoxy.

35 R₂₄ is a group -N(R₁)₂ or -N(R₈)₂R₉-A' or a group -CO-Y₂-Z', -NHCO-Y₂-Z', . . . -CONH-Y₂-Z', -SO₂NH-Y₂-Z'; -Y₂-Z' or -NHNHCOCH₂-Z'
where Y₂ is C₁-alkylene 35

7. A compound according to Claim 6 in which B is B'' where B'' is $-A''-NH-R_2''$, hydrogen,

-CH₃, -C₂H₅, benzyl; -(CH₂)₆N(R₇'')₂; and -(CH₂)_bN(R₈'')₂R₉'' A'' where b is 2 or 3; 40 A'' is 1,2-ethylene, 1,3-propylene or unsubstituted meta or para phenylene. 40

R₂" is hydrogen, methyl, ethyl or 2-hydroxyethyl or both R₂" is together with the N-atom to which they are attached form an unsubstituted morpholine, piperidine, piperazine or N-methylpiperazine group;

45 R_8'' is one of the significances of R_7'' except hydrogen and R_9'' is $-CH_3$, $-C_2H_5$ or benzyl or both R_8'' 's and R_9'' together with the N-atom to which they are attached form a pyridinium ring unsubstituted or substituted by one or two methyl groups or is a group β defined in Claim 6; R_2'' is 45



55 where q is defined in Claim 1;
R₁₁" is hydrogen, methyl or chloro;
R₁₂" is COCH₂Z" or



65 Z'' is $N(R_z'')_2$ or $-N(R_a'')_2 R_a'' A^-$

5 R₁₃'' is -N-R₂₁';



5 R₁₄'' is -N-R₂₁';



10 R₂₁' is -(CH₂)₂₋₃-N(R₇'')-(CH₂)₂₋₃-N(R₇'')R₆'

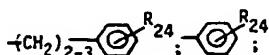
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-(CH₂)₂₋₃-N(R₈'')₂-(CH₂)₂₋₃-N(R₈'')₂R₆' A'

-(CH₂)₂₋₃-N(R₇'')-C₂H₅

15 -(CH₂)₂₋₃-N(R₈'')₂-C₂H₅;

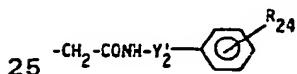
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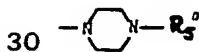
20 -NHCOCH₂-Z''

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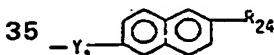
-CH₂-CONH-Y₂'-Z''; Y₂'-Z'';



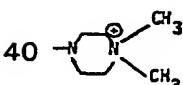
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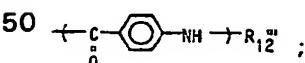


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where R₆' is methyl or ethyl, R₂₄ is defined in Claim 6, and Y₂' is (C₁₋₄)alkylene.

8. A compound according to Claim 6 or Claim 7 in which B is B''' where B''' is CH₃, C₂H₅, 45 benzyl, -(CH₂)₂₋₃-N(R₇'')₂, -(CH₂)₂₋₃-N(R₈'')₂R₉ A' or -A''-NH-R₂'''; where A'', R₇'' and R₉'' are defined in Claim 7; R₂''' is

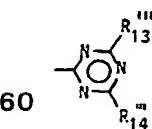
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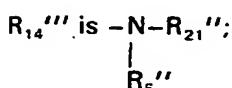
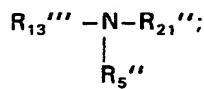
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55 R₁₂''' is

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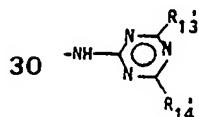


10 R_{21}'' is $NHCOCH_2 - Z'', -(CH_2)_{2-3} - Z'',$



where R_{24}' is $-N(CH_3)_2$, $-\bar{N}(CH_3)_3 A^9$; $-CONH(CH_2)_{2-3}Z''$, $-NHCO(CH_2)_{2-3} - Z''$, $-CO(CH_2)_{2-3} - Z''$, or $SO_2NH(CH_2)_{2-3} Z''$; and Z'' is defined in Claim 7.

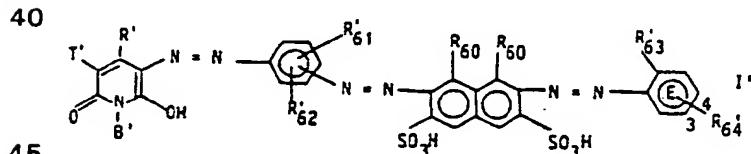
20 9. A compound according to any one of the preceding claims in which R_{62} is R_{62}' where R_{62}' is hydrogen, chloro, nitro, methyl, methoxy or OH; 20
 R_{61} is R_{61}' where R_{61}' is hydrogen, methoxy or methyl; and
 R_{63} is R_{63}' where R_{63}' is hydrogen, nitro, methoxy, ethoxy, OH, methyl, ethyl or chloro.
 10. A compound according to any one of the preceding claims in which R_{64} is R_{64}' where
 25 R_{64}' is 25



35 $N - (R_7')_2$, $-\bar{N}(R_8')_2 R_9' A^+$, $-CONH - Y_2' - Z'$, $-CO - Y_2' - Z$, $-Y_2' - Z'$, $-SO_2NHY_2' - Z -$, $-NHCOY_2' - Z'$, $NHNHCOCH_2 - Z'$; 35

where R_7' , R_8' , R_9' and Z' , are defined in Claim 6 and Y_2' is defined in Claim 7.

11. A compound according to Claim 1 in metal-free, 1:1 or 1:2 metal complex form or in free acid or acid addition salt form, of formula I'



45 in which R' is defined in Claim 2;
 T' is defined in Claim 4;

50 B' is defined in Claim 6;

R_{60}' is defined in Claim 1;

R_{64}' is defined in Claim 10; and

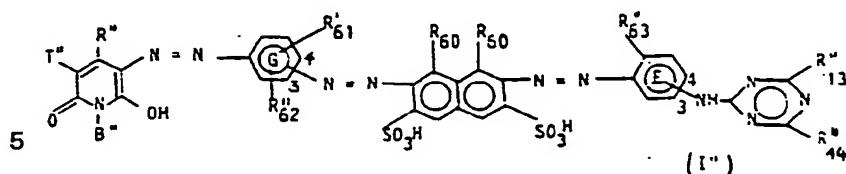
R_{61}' , R_{62}' and R_{63}' are defined in Claim 9;

with the provisos that:

55 (i) the number of cationic and protonatable basic groups exceeds the number of sulphonate groups present by at least one;

(ii) that R_{64}' is in the 3- or 4-position on the phenyl ring to which it is attached (the positions being as indicated).

12. A compound according to Claim 1, in metal-free, 1:1 or 1:2 metal complex form or in acid free or acid addition salt form, of formula I''



in which R_{62}'' is hydrogen, chloro or methyl;

R_{63}'' is hydrogen, OH or methoxy;

R_{60} is defined in Claim 1;

10 R'' is defined in Claim 3;

10

T'' is defined in Claim 5,

B'' , R_{13}'' and R_{14}'' are defined in Claim 7;

with the provisos that:

(i) the number of cationic and protonatable basic groups exceeds the number of sulpho

15 groups present by at least one;

15

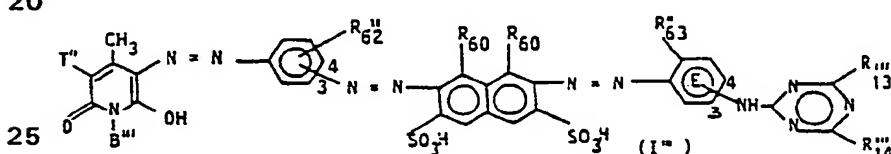
(ii) that the amino group on ring E is in the 3- or 4-position (the positions being as indicated);

(iii) that the azo group on ring G is in the 3- or 4-position (the positions being as indicated).

13. A compound according to Claim 1, in metal-free, 1:1 or 1:2 metal complex form or in free acid or acid addition salt form, of formula I'''

20

20



in which T'' is defined in Claim 5;

R_{62}'' is defined in Claim 12;

R_{60} is defined in Claim 1;

30 B''', R_{13}''' and R_{14}''' are defined in Claim 8;

30

with the provisos that

(i) the number of cationic and protonatable basic groups exceeds the number of sulpho groups present by at least one;

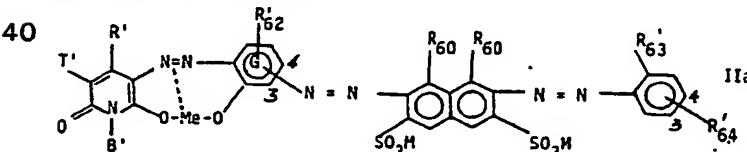
(ii) that the amino group on ring E is in the 3- or 4-position (the positions being as

35 indicated);

35

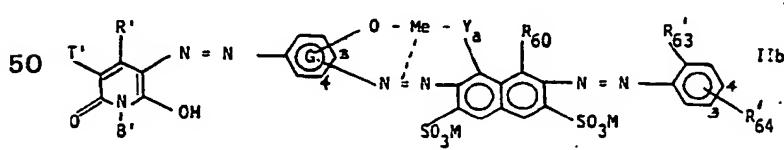
(iii) that the azo group on ring G is in the 3- or 4-position (the positions being as indicated).

14. A compound according to Claim 1, in 1:1 or 1:2 metal complex form and in free acid or acid addition salt form, of formula IIa to IIc

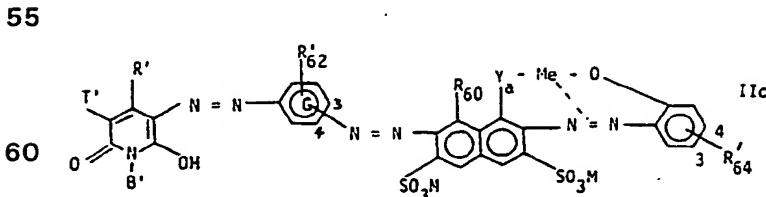


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in which R' is defined in Claim 2;

T' is defined in Claim 4;

B' is defined in Claim 6;

R₆₂' is defined in Claim 9;

5 R₆₀ is defined in Claim 1;

R₆₃' is defined in Claim 9;

R₆₄' is defined in Claim 10;

Y_a is -O- or -NH-;

Me is copper, chromium, cobalt, nickel, iron, manganese or zinc when in 1:1 metal complex form or Me is chromium, cobalt, iron or nickel when in 1:2 metal complex form;

with the provisos that:

(i) in the compounds of formula IIa, IIb and IIc R₆₄' is in the 3- or 4-position, the naphthyl azo group on ring G is in the 3- or 4-position and the number of cationic and protonatable basic groups present exceeds the number of sulpho groups present;

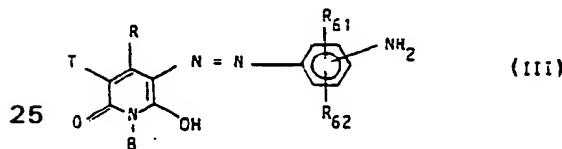
15 15 (ii) in the compounds of formula IIb the group -O-Me-Ya to the naphthyl azo group; and

(iii) in the compounds of formula IIb and IIc when Y_a is -NH- then R₆₀ is OH and when Y_a is -O- then R₆₀ is NH₂.

15. A process for preparing a compound according to Claim 1 comprising

(1) reacting a diazotised compound of formula III

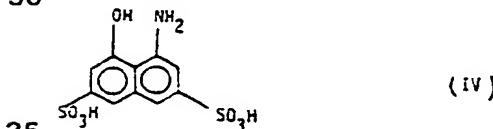
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with a compound of the formula IV

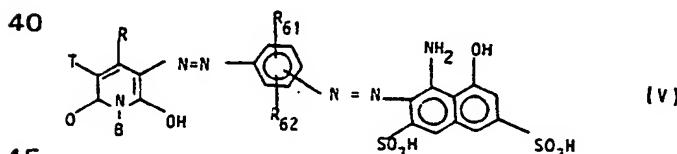
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in acid medium to form a compound of formula V

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followed by reacting the compound of formula V with a diazotised compound of formula VI

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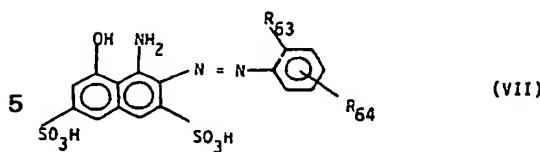


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55 in alkali medium, and

optionally metallising the resulting product; or

(2) reacting a diazotised compound of formula VI with the compound of formula IV to form a compound of formula VII



5 in acid medium followed by reacting the compound of formula VII with a diazotised compound
10 of formula III in alkali medium; and
optionally metallising the resulting product.

16. A process for dyeing a substrate comprising applying to that substrate a compound of
formula I defined in Claim 1.

17. A compound of formula I defined in Claim substantially as herein described with
15 reference to any one of Examples 1 to 28.

18. A process according to Claim 16 substantially as herein described with reference to any
one of Application Examples A to E.

19. Textile material to which a compound of formula I defined in Claim 1 has been applied.

20. Paper or leather to which a compound of formula I defined in Claim 1 has been applied.

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